TECHNICAL TRANSACTIONS 2/2018
CHEMISTRY
DOI: 10.4467/2353737XCT.18.025.7998
SUBMISSION OF THE FINAL VERSION: 10/1/2018

Przemysław Woliński
Agnieszka Kącka-Zych (akacka@chemia.pk.edu.pl)
Faculty of Chemical Engineering and Technology, Cracow University of Technology

Chemistry of 2-aryl-1-cyano-1-nitroethenes. Part II. Chemical transformations

---

Chemia 2-arylo-1-cyjano-1-nitroetenów. Część II. Chemiczne transformacje

Abstract

This work is a continuation of our study on the chemistry of 2-aryl-1-cyano-1-nitroethenes. In this paper, we describe the reactivity of 2-aryl-1-cyano-1-nitroethenes as a key component in [2+3] and [2+4] cycloaddition reactions, and in other transformations.

Keywords: 2-aryl-1-cyano-1-nitroethene, [2+3] cycloaddition, [2+4] cycloaddition, transformations of 2-aryl-1-cyano-1-nitroethenes, ACN

Streszczenie

Praca stanowi kontynuację studiów dotyczących chemii 2-arylo-1-cyjano-1-nitroetenów. W jej ramach dokonaliśmy przeglądu transformacji 2-arylo-1-cyjano-1-nitroetenów jako komponentów [2+3], [2+4] cykloaddycji oraz w innych reakcjach.

Słowa kluczowe: 2-arylo-1-cyjano-1-nitroeten, [2+3] cykloaddycja, [2+4] cykloaddycja, transformacje 2-arylo-1-cyjano-1-nitroetenów

1. Introduction

The chemistry of substituted 2-aryl-1-cyano-1-nitroethenes (ACNs) is a promising field in modern organic chemistry and accessible compounds for preparation of various important organic components [1]. ACNs have been known since the first half of the twentieth century [2]. Currently, several compounds of this group are known; nonetheless, their chemical properties are not well recognized [3–6]. The chemical transformations of these compounds include [2+3] cycloaddition to nitrogen-containing Three-Atoms-Components (TACs), which occupies an important place among the synthetic tools of organic chemistry [7]. Several examples of the participation of ACNs in Diels-Alder reactions as ethylenes as well as heterodienes are also known [3, 8, 9].

This paper is a continuation of our study on the chemistry of 2-aryl-1-cyano-1-nitroethenes. In the previous paper we characterized the synthetic protocols as well as the physical description of the compounds studied. In turn this part of our study contains the chemical transformations of ACNs as a component in different types of reactions.

2. [2+3] cycloaddition reactions with 2-aryl-1-cyano-1-nitroethenes

Chemical transformations of substituted cyanonitroethenes include [2+3] cycloaddition reactions (1,3-dipolar cycloaddition) to nitrogen containing TACs, which occupies an important place among the synthetic tools of organic chemists. Formed as a result, nitrogen containing heterocycles demonstrates a broad spectrum of significant properties. In particular the 1,2,3-triazole rings constitute a structural fragment of a number of pharmaceuticals [1], photosensitizers [10], and optical bleaching agents [11].

In 2011, *Nosachev, Shchurova* and *Tyrkov* [7] presented a study of the [2+3] cycloaddition reactions of 2-phenyl-1-cyano-1-nitroethene (PCN) (**1**) with arylazides (**2a,b**). Reactions conducted in diethyl ether at room temperature gave a mixture of regioisomeric 1-aryl-4-nitro-5-phenyl-4,5-dihydro-1H-1,2,3-triazole-4-carbonitriles (**3a,b**) and 1-aryl-5-nitro-4-phenyl-4,5-dihydro-1H-1,2,3-triazole-5-carbonitriles (**5a,b**). Finally, 1-aryl-5(4)-phenyl-1H-1,2,3-triazole-4(5)-carbonitriles (**4a,b**, **6a,b)** (Table 1) were formed as a result of spontaneous nitrous acid extrusion from primary [2, 3] cycloaddition products [7].

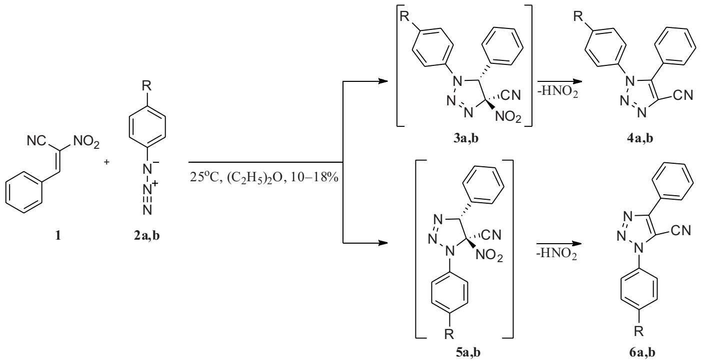


Table 1. Synthesis of 1-aryl-5(4)-phenyl-1H-1,2,3-triazole-4(5)-carbonitriles (**4a,b**, **6a,b**) from PCN (**1**) and arylazides (**2a,b**) [7]

Entry	Azide	R	Product	Yield [%]
1	**2a**	H	**4a**	15
2	**2b**	CH_3	**4b**	18
3	**2a**	H	**6a**	10
4	**2b**	CH_3	**6b**	10

Piet et al [12] also deal with the [2+3] cycloaddition reactions of PCN (**1**) with phenylazide (**2a**) and methylazide (**7**). They obtained 1-methyl-5-phenyl-1H-1,2,3-triazole-4-carbonitrile (**9**) and 1-methyl-4-phenyl-1H-1,2,3-triazole-5-carbonitrile as a result (**11**). In the case of 1,5-diphenyl-1H-1,2,3-triazole-4-carbonitrile (**4a**) and 1,4-diphenyl-1H-1,2,3-triazole-5-carbonitrile (**6a**) the authors do not present the quantities of the compounds obtained (Table 2).

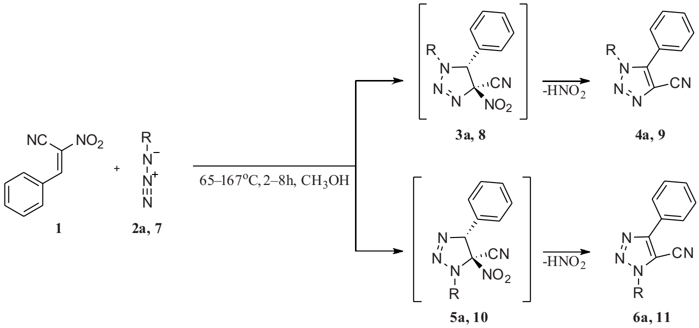


Table 2. Synthesis of 1-methyl-5(4)-phenyl-1H-1,2,3-triazole-4(5)-carbonitrile (**9**)(**11**) and 1,5(4)-diphenyl-1H-1,2,3-triazole-4(5)-carbonitrile (**4a**)(**6a**) [12]

Entry	Azide	R	Product	Ratio
1	**2a**	C_6H_5	**4a:9a**	–
2	**7**	CH_3	**9:11**	0.13

Likewise, *Amantini* et al [13] described the synthesis of 4-aryl-1H-1,2,3-triazole-5-carbonitriles (**15a-g**) through tetrabutylammonium fluoride (TBAF) catalysed [2+3] cycloaddition of (E)-ACNs (**1**, **12a-f**) with azido(trimethyl)silane (**13**). These reagents subsequently experienced aromatization and [1.3]–sigmatropic hydrogen shift, leading to 4-aryl-1H-1,2,3-triazole-5-carbonitriles (**15a-g**) with excellent yield (Table 3).

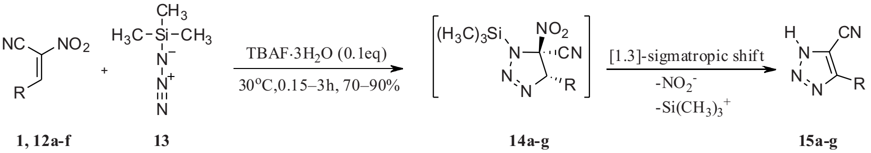
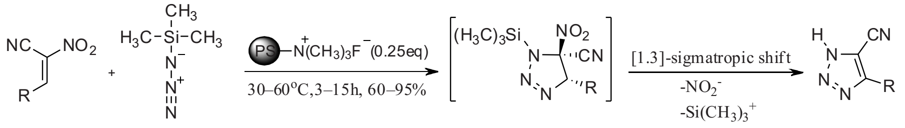


Table 3. Synthesis of 4-aryl-1H-1,2,3-triazole-5-carbonitriles (**15a-g**) through TBAF catalyzed [2+3] cycloaddition [13]

Entry	ACN	R	Time [h]	Product	Yield [%]
1	**1**	C_6H_5	3	**15a**	85
2	**12a**	(4-Cl)-C_6H_4	0.15	**15b**	90
3	**12b**	(4-OCH_3)-C_6H_4	3	**15c**	75
4	**12c**	(4-OH)-C_6H_4	3	**15d**	70
5	**12d**	(3,4-OCH_2O)-C_6H_3	1	**15e**	85
6	**12e**	2-furyl	2	**15f**	75
7	**12f**	2-thienyl	3	**15g**	75

Another example of catalysed [2+3] cycloadditions are the reactions investigated by *Fringuelli's* group [14]. The catalysed process was the reaction between (E)-ACNs (**1**, **16a-e**) and azido(trimethyl)silane (**13**) carried out in the presence of Amberlite IRA900F (Amb-F). These reactions are used for the preparation of 4-aryl-1H-1,2,3-triazole-5-carbonitriles (**15a**, **18a-e**); however, the reaction yield is 60-95% (Table 4).



1, 16a-e **13** **14a, 17a-e** **15a, 18a-e**

Table 4. Synthesis of 4-aryl-1H-1,2,3-triazole-5-carbonitriles (**15a**, **18a-e**) in the presence of Amb-F [14]

Entry	ACN	R	T [°C]	Time [h]	Product	Yield [%]$^{(a)}$
1	**1**	C_6H_5	30	3	**15a**	95
2	**1**	C_6H_5	30	9	**15a**	$93^{(b)}$
3	**1**	C_6H_5	30	3	**15a**	$82^{(c)}$
4	**1**	C_6H_5	30	3	**15a**	$83^{(d)}$
5	**1**	C_6H_5	30	3	**15a**	$60^{(e)}$
6	**1**	C_6H_5	30	3	**15a**	$94^{(f)}$
7	**1**	C_6H_5	30	3	**15a**	$95^{(f)}$
8	**16a**	(2-OCH_3)C_6H_4	60	12	**18a**	92
9	**16b**	(2,4-OCH_3)C_6H_3	60	15	**18b**	90
10	**16c**	(2,4,6-CH_3)C_6H_2	60	14	**18c**	90
11	**16d**	(2,4-Cl)C_6H_3	60	12	**18d**	75
12	**16e**	(2-Cl-6-F)C_6H_3	60	12	**18e**	80

(a) 3.0 eq. of azido(trimethyl)silane (**13**) (b) 0.10 eq. Amb-F. (c) Reaction in 2 ml/mmol of THF. (d) Reaction in 2 ml/mmol of DCE. (e) 0.10 eq. TBAF. (f) Reaction with recovered Amb-F.

Nosachev et al [15] presented the studies of [2+3] cycloaddition of PCN (**1**) to N-phenacyl- (**19a**) or N-acetonyl- (**19b**) isoquinolinium bromides. Those reactions provide an interesting pathway to the hardly accessible isoquinolines (**21a,b**) in high to excellent yield and full regioselective manner. The authors also obtained 1-nitro-2,3-diphenyl- (**22a**) and 3-methyl-1-nitro-2-phenyl- (**22b**) 2,2a,5,5a,6,10b-hexahydro-1H-benzo[g][1,2,3]triazino-[5,4,3-cd]indolizine-1-carbonitriles resulting from the formation of intermediate hydrazine derivatives of pyrrolidine which undergo a spontaneous heterocyclization into compounds **22a,b** with 30-41% yield (Table 5) [15].

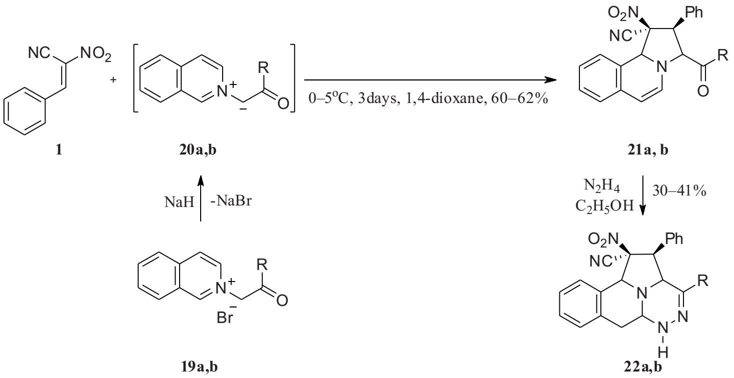


Table 5. Synthesis of isoquinolines (**21a,b**), 1-nitro-2,3-diphenyl- (**22a**) and 3-methyl-1-nitro-2-phenyl- (**22b**) 2,2a,5,5a,6,10b-hexahydro-1H-benzo[g][1,2,3]triazino-[5,4,3-cd]indolizine-1-carbonitriles [15]

Entry	Substrate	R	Product	Yield [%]	Product	Yield [%]
1	**19a**	C_6H_5	**21a**	60	**22a**	41
2	**19b**	CH_3	**21b**	62	**22b**	30

Recently published experimental and quantum-chemical studies confirm that reactions between (E)-ACNs (**1**, **12a,b**, **23**) and diazofluorene (**24**) lead to acyclic 2,3-diazabuta-1,3-diene derivatives (**27a-d**) (Table 6) instead of the expected pyrazoline systems [16]. The quantum-chemical calculations suggest that this could be a consequence of the formation of zwitterionic structures (**26a-d**) in the first reaction stage. The authors explained this as a specific property of the (E)-2-aryl-1-cyano-1-nitroethenes (**1**, **12a,b**, **23**) group.

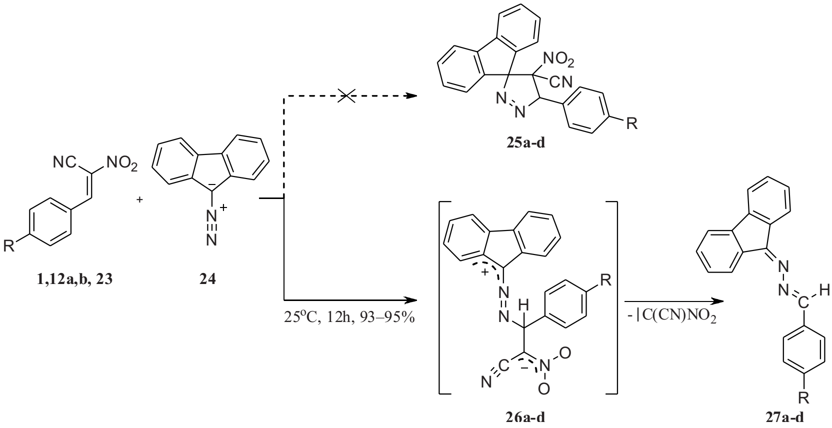


Table 6. Synthesis of 2,3-diazabuta-1,3-diene derivatives (**27a-d**) [16]

Entry	ACN	R	Product	Yield [%]
1	**1**	C_6H_5	**27a**	95
2	**12a**	$(4\text{-}Cl)\text{-}C_6H_4$	**27b**	93
3	**12b**	$(4\text{-}OCH_3)\text{-}C_6H_4$	**27c**	95
4	**23**	$(4\text{-}F)\text{-}C_6H_4$	**27d**	95

3. [2+4] cycloaddition reactions with 2-aryl-1-cyano-1-nitroethenes

Thanks to their specific structure, ACNs can undergo Diels-Alders reactions as a heterodiene component as well as dienophil one. This feature broadens their use significantly. As a result of these reactions biphenyl analogues, norbornenes and benzoxazines derivatives have been produced [7].

Jasiński et al [17, 18], conducted a series of reactions of ACNs (**1**, **12a,b**, **28a,b**) with cyclopentadiene (**29**) in nitromethane which lead to the formation of *endo*- and *exo*-nitronorbornenes (**30a-e**, **31a-e**). After 24 hours, almost full conversion was achieved and the products (**30a-e**, **31a-e**) (Table 7) were isolated by semipreparative HPLC.

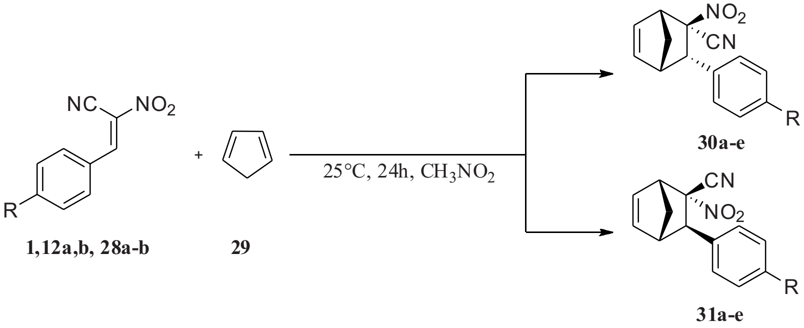


Table 7. Synthesis of nitronorbornenes (**30a-e**, **31a-e**) in nitromethane [17]

Entry	ACN	R	T [°C]	Products	30a-e:31a-e ratio
1	**1**	H	25	**30-31a**	0.14
2	**12a**	Cl	25	**30-31b**	0.15
4	**12b**	CH_3O	25	**30-31c**	0.08
3	**28a**	Br	25	**30-31d**	0.15
5	**28b**	$COOCH_3$	0	**30-31e**	0.17
6	**28b**	$COOCH_3$	25		0.19

Recently Łapczuk-Krygier et al [19] performed cycloaddition of ACNs (**1**, **12a,b**, **23**, **28b**, **32**) to cyclopentadiene (**29**) in ionic liquids. In comparison to the earlier study [17], the authors obtained cycloadducts (**30a-c**, **30e**, **33a,b**, **31a-c**, **31e**, **34a,b**) after only 10 minutes, and varying stereoselectivity which depended on the ionic liquid used (Table 8). They proposed this method as effective and eco-friendly.

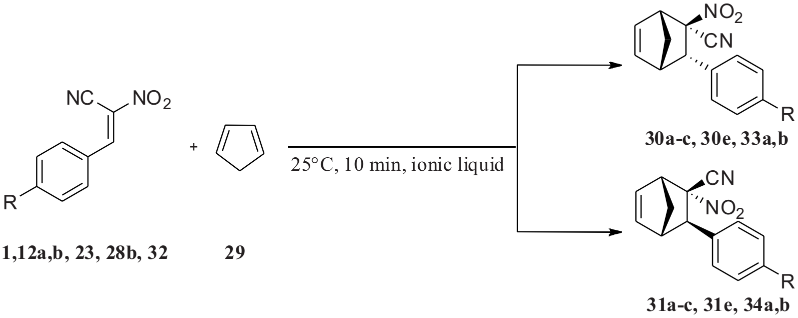


Table 8. Synthesis of nitronorbornenes (**30a-c**, **30e**, **33a,b**, **31a-c**, **31e**, **34a,b**) in ionic liquids [19]

Entry	ACN	R	Ionic liquid	Products	Products ratio
1	**1**	H	[BMIM][Cl]	**30a, 31a**	0.16
2		H	[TEAS]		0.16
3		H	[HMIM][HSO_4]		0.19
4		H	[C_6MIM][Cl]		0.14
5		H	[TEAP]		0.13
6		H	[BMIM][BF_4]		0.11
7	**12a**	Cl	[BMIM][Cl]	**30b, 31b**	0.17
8	**12b**	CH_3O	[BMIM][Cl]	**30c, 31c**	0.24
9	**23**	F	[BMIM][Cl]	**33a, 34a**	0.14
10	**28b**	$COOCH_3$	[BMIM][Cl]	**30e, 31e**	0.12
11	**32**	CH_3	[BMIM][Cl]	**33b, 34b**	0.13

Baichurin et al. [20] synthesized *gem*-cyanonitrocyclohexenes (**36a-d**) by cycloaddition of ACNs (**1**, **12b**, **12e-f**) to 2,3-dimetyl-1,3-butadiene (**35**). The reaction was performed in boiling toluene, and after 2-9 hrs the products were isolated with 54-94% yield (Table 9).

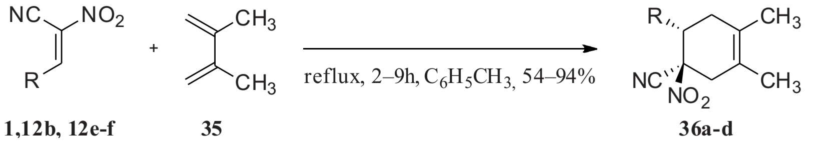


Table 9. Synthesis of *gem*-cyanonitrocyclohexenes (**36a-d**) in toluene [20]

Entry	ACN	R	Time [h]	Product	Yield [%]
1	**1**	C_6H_5	3	**36a**	75
2	**12b**	$(4\text{-}CH_3O)C_6H_4$	9	**36b**	94
3	**12e**	2-furyl	2	**36c**	54
4	**12f**	2-thienyl	4	**36d**	83

A series of 2-aryl-1-cyano-1-nitroethenes (**1**, **16b-d**, **32**, **37a-g**) have been used in cycloaddition to four different 1,3-butadienes (**35**, **38a-c**) by *Pizzo* et al [21]. They conducted the reactions in solvent free conditions and generated *in situ* obtaining very good yields (75–88%) of cycloadducts (**39a-n**). Aromatization of (**39a-n**) was achieved by reaction with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in the presence of O_2. Biphenyls (**40a-n**) were isolated in 45-80% yield (Table 10).

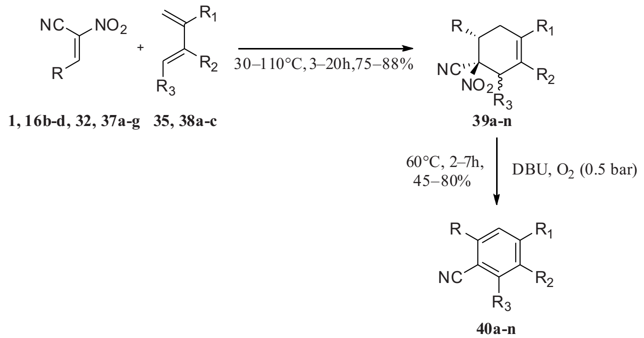
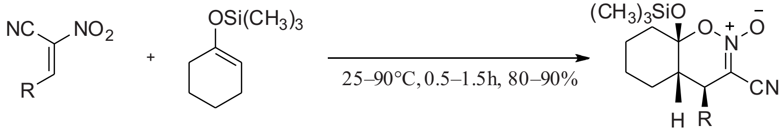


Table 10. Synthesis of cycloadducts (**39a-n**) and biphenyls (**40a-n**) in solvent-free conditions [21]

Entry	ACN	R	Diene	R_1, R_2, R_3	T [°C]	Time [h]	Yield of 39 [%]	Time [h]	Yield of 40 [%]
1	**1**	C_6H_5	**35**	$R_1=R_2=CH_3$, $R_3=H$	60	5	86	3	75
2		C_6H_5	**38a**	$R_1=R_2=H$, $R_3=CH_3$	60	10	85	5	65
3		C_6H_5	**38b**	$R_1=CH_3$, $R_2=R_3=H$	60	12	80	4	70
4	**16b**	(2,4-CH_3O)C_6H_3			30	12	80	5	45
5	**16c**	(2,4,6-CH_3)C_6H_2			30	12	78	3	62
6	**16d**	(2,4-Cl)C_6H_3			60	6	84	5	70
7	**37a**	(2-CH_3)C_6H_4			60	6	85	6	57
8	**37b**	(2-CH_3O)C_6H_4			60	20	88	3	60
9	**37c**	(2-CF_3)C_6H_4			30	12	77	2.5	70
10	**37d**	(2-NO_2)C_6H_4			30	12	78	6	57
11	**37e**	(4-CN)C_6H_4			30	10	85	6	77
12	**37f**	(2-Cl-6-F)C_6H_3			60	12	82	2	70
13	**37g**	(3,5-Br-4-OH) C_6H_2			30	15	75	7	80
14	**32**	(4-CH_3)C_6H_4	**38c**	$R_1=R_2=R_3=H$	110	12	75	6	65

Vaccaro et al [22] presented an uncatalysed and solvent-free cycloaddition of ACNs (**1**, **12a-e**, **16b**, **32**, **37b**, **37d**, **41a,b**) to 1-(trimethylsilyloxy)-cyclohex-1-ene (**42**). The hexahydro-4*H*-1,2-benzoxazine-2-oxide (**43a-l**) formed was isolated with 80–90% yield (Table 11). The authors showed this reaction to be fully regio- and stereoselective.

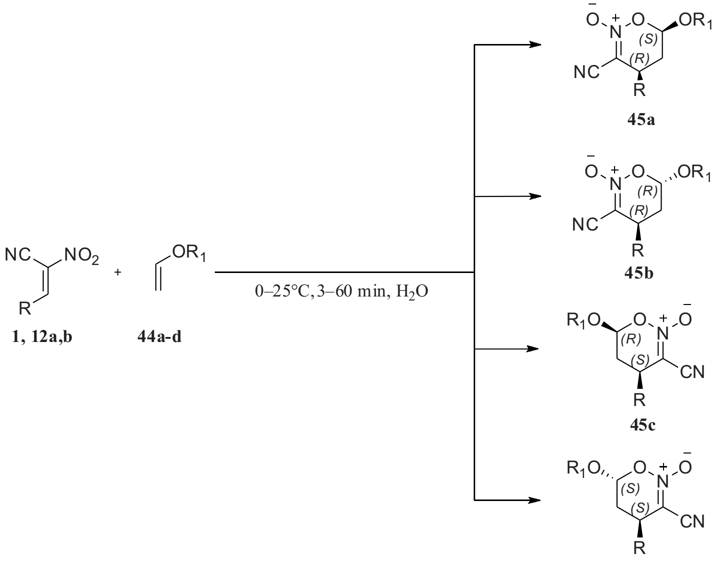


1, 12a-e, 16b, 32, 37b, 37d, 41a,b **42** **43a-l**

Table 11. Synthesis of hexahydro-4*H*-1,2-benzoxazine-2-oxides (**43a-l**) in solvent-free conditions [22]

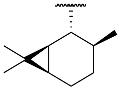
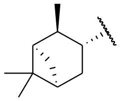
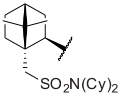
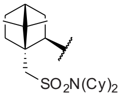
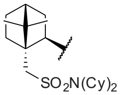
Entry	ACN	R	T [°C]	Time [h]	Product	Yield [%]
1	**1**	C_6H_5	25	0.75	**43a**	90
2	**12a**	$(4\text{-Cl})C_6H_4$	25	0.75	**43b**	90
3	**12b**	$(4\text{-}CH_3O)C_6H_4$	30	1.25	**43c**	90
4	**12c**	2-furyl	50	0.5	**43d**	86
5	**12d**	$(3,4\text{-}OCH_2O)C_6H_3$	60	0.5	**43e**	80
6	**12e**	2-thienyl	60	0.5	**43f**	84
7	**16b**	$(2,4\text{-}CH_3O)C_6H_3$	90	1.0	**43g**	80
8	**32**	$(4\text{-}CH_3)C_6H_4$	25	1.25	**43h**	85
9	**37b**	$(2\text{-}CH_3O)C_6H_4$	40	1.25	**43i**	87
10	**37d**	$(2\text{-}NO_2)C_6H_4$	30	1.0	**43j**	82
11	**41a**	$(4\text{-}CF_3)C_6H_4$	30	1.0	**43k**	80
12	**41b**	$(4\text{-}CH_3S)C_6H_4$	40	1.5	**43l**	85

In 2001 *Fringuelli* et al. [8] vinyl ethers were used (**44a-d**) in a cycloaddition reaction with ACNs (**1**, **12a,b**) in water. The yields of nitronates (**45a-d**) were very high (75-90%) but a mixture of diastereoisomers was obtained (Table 12). The kinetic aspects of these transformations have also been recently discovered [9]

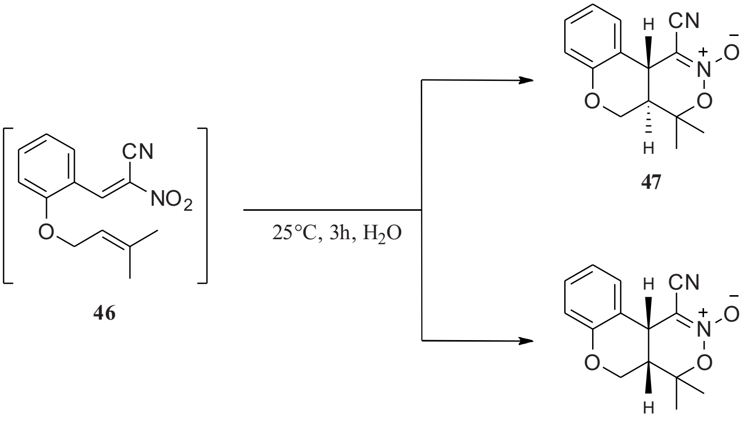


1, 12a,b **44a-d** **45a** **45b** **45c** **45d**

Table 12. Synthesis of nitronates (**45a-d**) in water [8]

Entry	**ACN**	**R**	**R_1**	**T [°C]**	**Time [min]**	**Isomer 45 [%]**				**Yield [%]**
						a	**b**	**c**	**d**	
1	**1**	C_6H_5	C_2H_5	0	3	80	20	–	–	75
2	**12a**	$(4–Cl)C_6H_4$	C_2H_5	0	20	96	4	–	–	90
3	**12b**	$(4–CH_3O)C_6H_4$	C_2H_5	25	10	98	2	–	–	85
4	**12a**	$(4–Cl)C_6H_4$		0	30	35	6	54	5	–
5	**12a**	$(4–Cl)C_6H_4$		0	30	30	5	60	5	–
6	**1**	C_6H_5		25	60	–	–	85	15	–
7	**12a**	$(4–Cl)C_6H_4$		0	60	–	–	85	15	–
8	**12b**	$(4–CH_3O)C_6H_4$		25	60	–	–	83	17	–

In the same year, *Pizzo* et al [3] showed an example of intramolecular cycloaddition in 2-(2'-(3",3"-dimethyl)allyloxyphenyl)-1-cyano-1-nitroetene (**46**) generated *in situ*. This reaction led to the formation of *cis*-4a,10b,-dihydro-1-cyano-4,4,dimethylbenzo[*b*]pyrene- [4,3-*d*][1,2] oxazine-2-oxide (**47**) and its 4a-epimer (**48**) in a 16:1 ratio and with a 60% yield of (**48**).



46

47

48

4. Other transformations with 2-aryl-1-cyano-1-nitroethenes

In 1999, *Kislyi* et al [23], found that ACNs (**1**, **12a,b**, **23**) react with cyclohexane-1,3-dione (**49**) or 5,5-dimethylcyclohexane-1,3-dione (**51**) in the presence of catalytic amounts of triethylamine forming 2-amino-3-nitropyrans (**50a-d**, **52a-d**) with good yields (Table 13).

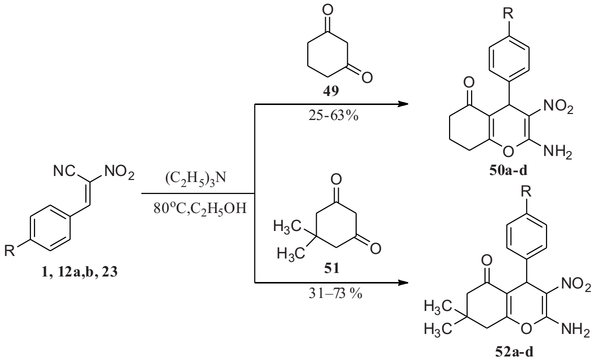


Table 13. Synthesis of 2-amino-3-nitropyrans (**50a-d**, **52a-d**) in the presence of $(C_2H_5)_3N$ [23]

Entry	ACN	R	Product	Yield [%]
1	**1**	H	**50a**	62
2	**12a**	Cl	**50b**	25
3	**12b**	CH_3O	**50c**	63
4	**23**	F	**50d**	30
5	**1**	H	**52a**	73
6	**12a**	Cl	**52b**	31
7	**12b**	CH_3O	**52c**	65
8	**23**	F	**52d**	42

The authors continued work and presented the syntheses of 2-amino-3-nitropyranol-[3,2-c]pyrans (**55a-c**) and 2-amino-3-nitropyranol[3,2,c]chromenes (**57a-c**). These products were obtained with 30-85% yield (Table 14) [24].

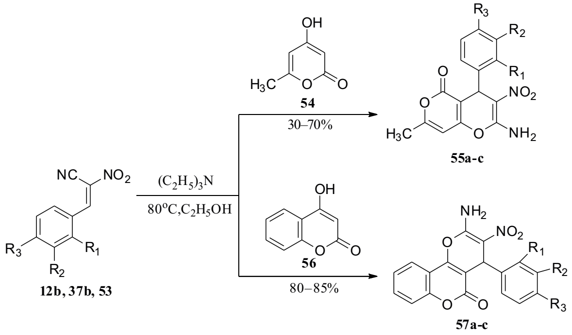
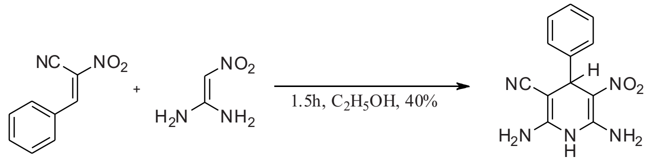


Table 14. Synthesis of 2-amino-3-nitropyranol-[3,2-c]pyrans (**55a-c**) and 2-amino-3-nitropyranol[3,2,c] chromenes (**57a-c**) [24]

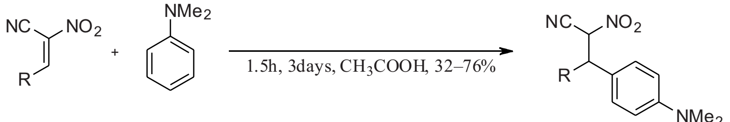
Entry	ACN	R_1	R_2	R_3	Product	Yield [%]
1	**12b**	H	H	CH_3O	**55a**	65
2	**37b**	CH_3O	H	H	**55b**	30
3	**53**	H	CH_3O	H	**55c**	70
4	**12b**	H	H	CH_3O	**57a**	85
5	**37b**	CH_3O	H	H	**57b**	80
6	**53**	H	CH_3O	H	**57c**	80

In turn, *Troschutz* and *Luckel* [25] used the PCN (**1**) to synthesize 2,6-diamino-1,4-dihydro-3,5-dinitro-4-phenylpyridine (**58**). They obtained product (**59**) with 40% yield.



1 **58** **59**

Baichurin et al [26] conducted reactions to prepare 3-(4-dimethylaminophenyl)-2-nitro-4-aryl-propanenitrile (**61a-c**) from 2-aryl-1-cyano-1-nitroethene (**1, 12b, 12f**) and N,N-dimethlaniline (**60**). The reactions were carried out at room temperature in acetic acid and led to compounds (**61a-c**) with 32–76% yields (Table 15).

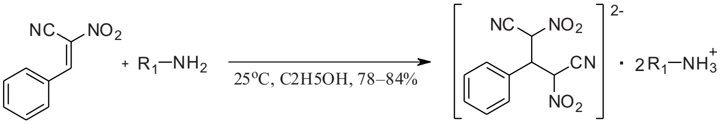


1, 12b, 12f **60** **61a-c**

Table 15. Synthesis of 3-(4-dimethylaminophenyl)-2-nitro-4-aryl-propanenitrile (**61a-c**) [26]

Entry	ACN	R	Product	Yield [%]
1	**1**	C_6H_5	**61a**	75
2	**12b**	$(4\text{-}CH_3O)C_6H_4$	**61b**	76
3	**12f**	2-thienyl	**61c**	32

The reactions of PCN (**1**) with aliphatic and heterocyclic amines with the lowest molecular weights were presented by *Demireva* et al. [27]. They obtained bis-alkylammonium salts of 2,4-dinitro-3-phenylglutarodinitrile (**63a-d**) with 78–84% yields (Table 16).

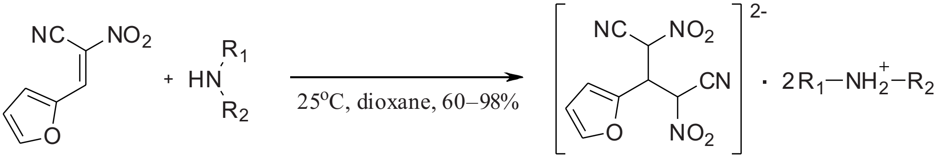


1 **62a-d** **63a-d**

Table 16. Synthesis of bis-alkylammonium salts of 2,4-dinitro-3-phenylglutarodinitrile (**63a-d**) [27]

Entry	**Amine**	**R_1**	**Product**	**Yield [%]**
1	**62a**	C_7H_{15}	**63a**	80
2	**62b**	C_8H_{17}	**63b**	82
3	**62c**	$C_{17}H_{35}$	**63c**	84
4	**62d**	$C_5H_{11}N$	**63d**	78

In 1984, *Metchkov* and *Demireva* [28] obtained a series of bis(ammonium) salts of 2,4-dinitro-3-(2-furyl)glutarodinitrile (**65a-j**) (Table 17) from 1-nitro-1-cyano-2-(2-furyl) ethane (**12e**) and aliphatic and alicyclic amines (**62b,c, 64a-h**)

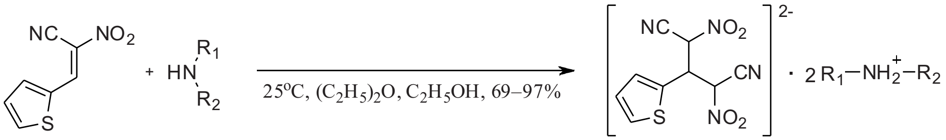


12e **62b,c, 64a-h** **65a-j**

Table 17. Synthesis of bis(ammonium) salts of 2,4-dinitro-3-(2-furyl)glutarodinitrile (65a-j) [28].

Entry	**Amine**	**R_1**	**R_2**	**Product**	**Yield [%]**
1	**64a**	H	n-C_3H_7	**65a**	98
2	**64b**	H	n-C_4H_9	**65b**	96
3	**64c**	H	$C(CH_3)_3$	**65c**	60
4	**64d**	H	C_6H_{12}	**65d**	80
5	**62b**	H	C_8H_{17}	**65e**	71
6	**64e**	H	$C_{12}H_{26}$	**65f**	71
7	**64f**	H	$C_{16}H_{33}$	**65g**	73
8	**62c**	H	$C_{17}H_{35}$	**65h**	75
9	**64g**	C_2H_5	C_2H_5	**65i**	83
10	**64h**	-$(CH_2)_5$-		**65j**	83

The same authors [29] presented a synthesis of a series of bis(ammonium) salts of 2,4-dinitro-3-(2-thiophene)glutarodinitrile (**66a-j**). They obtained products (**66a-j**) with good yields, reaching up to 97% (Table 18).

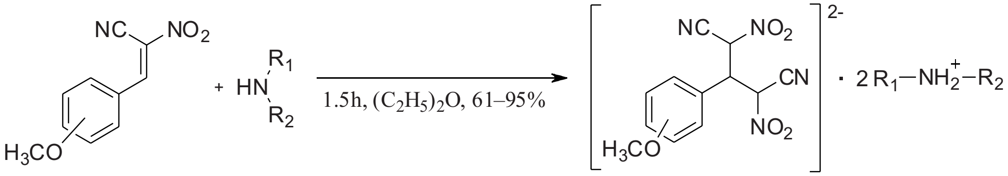


12f **62b,c, 64a-h** **66a-j**

Table 18. Synthesis of bis(ammonium) salts of 2,4-dinitro-3-(2-thiophene)glutarodinitrile (**66a-j**) [29]

Entry	Amine	R_1	R_2	Product	Yield [%]
1	**64a**	H	n-C_3H_7	**66a**	88
2	**64b**	H	n-C_4H_9	**66b**	97
3	**64c**	H	$C(CH_3)_3$	**66c**	97
4	**64d**	H	C_6H_{12}	**66d**	95
5	**62b**	H	C_8H_{17}	**66e**	80
6	**64e**	H	$C_{12}H_{26}$	**66f**	69
7	**64f**	H	$C_{16}H_{33}$	**66g**	82
8	**62c**	H	$C_{17}H_{35}$	**66h**	76
9	**64g**	C_2H_5	C_2H_5	**66i**	96
10	**64h**	$-(CH_2)_5-$		**66j**	52

The authors also showed the synthesis of bis(ammonium) salts of 2,4-dinitro-3-(methoxyphenyl)glutarodinitrile (**68a-j**) with 61–95% yields (Table 19) [30].



12b, 37b, 53 **64b, 64d, 64i, 67** **68a-f**

Table 19. Synthesis of bis(ammonium) salts of 2,4-dinitro-3-(methoxyphenyl)glutarodinitrile (**68a-f**) [30]

Entry	ACN	Amine	R_1	R_2	Product	Yield [%]
1	2-OCH_3 (**37b**)	**67**	H	H	**68a**	70
2	3- OCH_3 (**53**)	**67**	H	H	**68b**	61
3	4- OCH_3(**12b**)	**67**	H	H	**68c**	77
4	2-OCH_3(**37b**)	**64b**	H	C_4H_9	**68d**	95
5	3- OCH_3(**53**)	**64d**	H	C_6H_{11}	**68e**	92
6	4- OCH_3(**12b**)	**64i**	C_2H_5	C_2H_5	**68f**	76

5. Conclusion

A literature review demonstrated that 2-aryl-1-cyano-1-nitroethenes are mainly applied in the synthesis of carbo- and heterocyclic compounds. These compounds are especially used as ethylene in [2+4] cycloaddition reactions. We also noticed a few examples of [2+3] cycloaddition reactions involving 2-phenyl-1-cyano-1-nitroethenes. As we have shown, there are other examples of uses of ACNs transformations that are mainly involved in bis(ammonium) salts.

References

[1] Grimmett M.R., *Comprehensive Organic Chemistry*, Eds. D. Barton, W.D. Ollis, Pergamon, Oxford 1979, 4, 357–410.

[2] Ried W., Köhler E., Königstein F.J., *Reaktionen mit Nitro-acetonitril*, Liebigs Annalen der Chemie, 1956, 598, 145–148.

[3] Amantini D., Fringuelli F., Piermatti O., Pizzo F., Vaccaro L., *Water, a clean, inexpensive, and re-usable reaction medium. One-pot synthesis of (E)-2-aryl-1-cyano-1-nitroethenes*, Green Chemistry, 2001, 3, 229–232.

[4] Boguszewska-Czubara A., Łapczuk-Krygier A., Rykała K., Biernasiuk A., Wnorowski A., Popiołek Ł., Maziarka A., Hordyjewska A., Jasiński R., *Novel synthesis scheme and in vitro antimicrobial evaluation of a panel of (E)-2-aryl-1-cyano-1-nitroethenes*, Journal of Enzyme Inhibition and Medicinal Chemistry, 2015, 31, 900–907.

[5] Valizadeh H., Mamaghani M., Badrian A., *Effect of Microwave Irradiation on Reaction of Arylaldehyde Derivatives with Some Active Methylene Compounds in Aqueous Media*, Synthetic Communications, 2005, 35, 785–790.

[6] Jasiński R., Mirosław B., Demchuk O.M., Babyuk D., Łapczuk-Krygier A., *In the search for experimental and quantumchemical evidence for zwitterionic nature of (2E)-3-[4-(dimethylamino)phenyl]-2-nitroprop-2-enenitrile – An extreme example of donor–π–acceptor push–pull molecule*, Journal of Molecular Structure, 2016, 1108, 689–697.

[7] Nosachev S.B., Shchurova N.A., Tyrkov A.G., *Reactions of 2-Benzylidenemalononitrile and 2-Nitro-3-phenyl-acrylonitrile with Aryl Azides*, Russian Journal of Organic Chemistry, 2011, 47, 577–580.

[8] Fringuelli F., Matteucci M., Piermatti O., Pizzo F., Burla M.C., *[4 + 2] Cycloadditions of Nitroalkenes in Water. Highly Asymmetric Synthesis of Functionalized Nitronates*, Journal Organic Chemistry, 2001, 66, 4661–4666.

[9] Jasiński R., Kubik M., Łapczuk-Krygier A., Kącka A., Dresler E., Boguszewska-Czubara A., *An experimental and theoretical study of the hetero Diels–Alder reactions between (E)-2-aryl-1-cyano-1-nitroethenes and ethyl vinyl ether: one-step or zwitterionic, two-step mechanism?*, Reaction Kinetics, Mechanisms and Catalysis, 2014, 113, 333–345.

[10] Varma R.S., Kabalka G.W., *Nitroalkenes in the Synthesis of Heterocyclic Compounds*, Heterocycles, 1986, 24, 2645–2677.

[11] Padwa A., Pearson W.M., *Synthetic applications of 1,3-dipolar cycloaddition chemistry toward heterocycles and natural products*, Wiley&Sons, 2002.

[12] Piet J.C., Hetet G.L., Cailleux P., Benhaoua H., Carrier R.,*Reactions des methylazide et phenylazide avec quelquesalcynes et olefins α-nitrees. Syntheseregiospecifique des 1,2,3 triazoles*, Bulletin des Sociètès Chimiques Belges, 1996, 105, 33–44.

[13] AmantiniD., Fringuelli F.,PiermattiO., Pizzo F., Zunino E., Vaccaro L.,*Synthesis of 4-Aryl-1H-1,2,3-triazoles through TBAF-Catalyzed [3+2] Cycloaddition of 2-Aryl-1-nitroethenes with $TMSN_3$ under Solvent-Free Conditions*, The Journal of the Organic Chemistry, 2005, 70, 6526–6529.

[14] Friguelli F., Lanari D., Pizzo F., Vaccaro L., *Amberlite IRA900F as a Solid Fluoride Source for a Variety of Organic Transformations under Solvent-Free Conditions*, European Journal of Organic Chemistry, 2008, 23, 3928–3932.

[15] Nosachev S.B., Del'netskaya K.A., Solov'ev N.A., Tyrkov A.G., *Substituted 1-nitro-2-phenylethenes in reaction with N-phenacyl- and N-acetonylisoquinolinium bromides*, Russian Journal of Organic Chemistry, 2010, 46, 1427–1429.

[16] Jasiński R., Kula K., Kącka A., Mirosław B., *Unexpected course of reaction between (E)-2-aryl-1-cyano-1-nitroethenes and diazafluorene: why is there no 1,3-dipolar cycloaddition?*, Monatschefte für Chemie, 2017, 148, 909–915.

[17] Jasiński R., Rzyman M., Barański A., *Conjugated nitroalkenes in cycloaddition reactions. Part 2. Diels-Alder reactions of E-2-aryl-1-cyano-1-nitroethenes with cyclopentadiene*, Collection of Czech Chemical Communications, 2010, 75, 919–929.

[18] Łapczuk-Krygier A., Ponikiewski Ł., Jasiński R., *The crystal structure of (1RS,4RS,5RS,6SR)-5-cyano-5-nitro-6-phenyl-bicyclo[2.2.1]hept-2-ene*, Crystallography Reports, 2014, 59, 961–963.

[19] Łapczuk-Krygier A., Dresler E., Jasiński R., *Ionic liquids as an effective and eco-friendly medium for synthesis of nitrosubstitutednorborenes analogs*, Przemysł Chemiczny, 2016, 95, 1928–1931.

[20] Baichurin R. I., Aboskalova N. I., Trukhin E. V., Berestovitskaya V. M., *Aryl(hetaryl)-Containing gem-Cyanonitroethenes: Synthesis, Structure, and Reactions with 2,3-Dimethyl-1,3-butadiene*, Russian Journal of General Chemistry, 2015, 85, 1845–1854.

[21] Fringuelli F., Girotti R., Piermatti O., Pizzo F., Vaccaro L., *Uncatalyzed and sol vent-free multicomponent process for the synthesis of biphenyl-2-carbonitrile derivatives*, Organic Letters, 2006, 8, 5741–5744.

[22] Bellachioma G., Castrica L., Fringuelli F., Pizzo F., Vaccaro L., *Catalyst- and solvent-free conditions as an environmentally benign approach to 2-aryl-3-cyano-hexahydro-4H-1,2-benzoxazine-2-oxides*, Green Chemistry, 2008, 10, 327–332.

[23] Kislyi V.P., Nesterov V.N., Shestopalov A.M., Semenov V.V., *Heterocycles with a beta-nitroenamineframent. 1. Synthesis of 2-amino-3-nitro-pyrans from nitroacetonitrile*, Russian Chemical Bulletin, 1999, 48, 1131–1134.

[24] Kislyi V.P., Nesterov V.N., Shestopalov A.M., Semenov V.V., *Heterocycles with a β-nitroenamine fragment. 2. Synthesis of 2-amino-3-nitropyrano[3,2-c]pyrans and 2-amino-3-nitropyrano[3,2,c]chromenes from nitroacetonitrile*, Russian Chemical Bulletin, 1999, 4896, 1135–1138.

[25] Troschütz R., Lückel A., *Nitroketenaminale, 7. Mitt.: Synthese von substituierten 2-Amino-3-nitropyridinen aus 1,3-Biselektrophilen und 2-Nitroethen-1,1-diamin*, Archiv der Pharmazic, 1992, 325, 785–789.

[26] Meichkov T.D., Demireva Z.I., *Synthesis of some bis(ammonium) salts of 2,4-dinitro-3-(2-furyl)glutarodinitrile*, Journal of Chemical and Engineering Data, 1984, 29, 483–484.

[27] Meichkov T.D., Demireva Z.I., Tonicheva E., *Synthese einigerbie-ammonium salze des 2,4-dinitro-3-(2-thienyl)glutaranitrllen*, Zeitschrift für Chemie, 1985, 25, 62–63.

[28] Demireva Z.I., Binev I.G., Juchnovski I.N., *A new, versatile acyl activating reagent for peptide synthesis: asymmetrically selective peptide synthesis by use of optically active 3-hydroxyhydantoin*, Tetrahedron Letters, 1976, 18, 1523–1526.

[29] Baichurin R.I., Aboskalova N.I., Turkhin E.V., Berestovitskaya V.M.,*Arylation of geminally activated nitroethenes*, Russian Journal of Organic Chemistry, 2013, 49, 67–69.

[30] Meichkov T.D., Demireva Z.I., *Die synthese einigerbie-ammonium salze des 2,4-dinitro-3-(methoxyphenyl)glutaranitrllen*, Zeitschrift für Chemie, 1985, 25, 169–170.